

Chemical Dynamics

Photoionization

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Chemical Reaction Dynamics of Highly Vibrationally Excited Molecular Ions

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Ion beams of H_2^+ in selected rovibrational states were produced using a novel high-resolution pulsed-field ionization–coincidence approach that substantially extends the range and selectivity of accessible molecular ion states. Reaction cross sections of the $\text{H}_2^+ + \text{Ne}$ proton transfer reaction were measured for vibrational quantum levels ranging from $v^+ = 1$ to 13 at a translational energy of 1.2 eV. The results are compared with quasi-classical trajectory (QCT) calculations. The QCT proton transfer cross sections are approximately a factor 2 lower than the observed cross sections from $v^+ = 1$ to 10. The discrepancy increases at higher vibrational levels where dissociation competes effectively with ion-molecule reaction.

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Excitation-Energy Dependence of Cu $L_{2,3}$ X-Ray Emission Spectra of Cu, Cu₂O and CuO

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INTRODUCTION

Cu metal and its oxides have recently attracted considerable attention for the study of the electronic structure of copper oxides based on the superconducting matters. The Cu L X-ray emission spectra of Cu metal and its oxides have been measured by many laboratories for studying the electronic structure of the valence bands and the effect of chemical bonding on the satellites structure of the main peak of Cu $L\alpha_{1,2}$ X-ray emission using usual X-ray source [1,2] and synchrotron radiation [3-5]. The incident photon energy dependence was measured for Cu $L_{2,3}$ satellites using synchrotron radiation [3-5]. Changes in the Cu $L_{2,3}$ X-ray emission spectra with Cu metal and its oxides have been measured using electron excitation by Fischer [6]. He found that relative intensity $L\beta_1/L\alpha_{1,2}$ significantly depends on the incident electron energy and the target. The relative intensity $L\beta_1/L\alpha_{1,2}$ decreases with increase of excitation energy and it increases considerably for the oxides as compared to the metals.

In the present experiment, we have measured excitation-energy-dependence of Cu $L_{2,3}$ X-ray emission spectra of Cu, Cu₂O and CuO using synchrotron radiation in order to study the effect of chemical bonding in the excitation and deexcitation processes of inner-shell electrons of Cu metal and its oxides.

EXPERIMENT

The Cu (99.99 %) foil sample and sintered Cu₂O (99.9 %) and CuO (99.9 %) samples were commercially obtained. The spectral measurements in the Cu L region of these samples were performed at the beamline BL-8.0.1 for X-ray emission and fluorescence yield (FY) X-ray absorption measurements and at BL-6.3.1 for total-electron yield (TEY) X-ray absorption measurements.

In order to determine the excitation energies, XA spectra were measured by total electron-yields measurements. The incident photon current was continuously monitored using a gold mesh in

front on the sample to normalize the XE spectra.

RESULTS AND DISCUSSION

Cu $L_{2,3}$ X-ray emission (XE) spectra of Cu, Cu_2O and CuO spectra were measured at ten different excitation energies from 930~934 eV, at the L_3 threshold energy, up to energies as high as 990 eV, above the L_2 threshold energy. Figure 1 shows Cu $L_{2,3}$ XE spectra normalized to the integrated photon flux, excited at specific energies. The spectra were measured at 930~934 eV (L_3 threshold), at 950~952 eV (L_2 threshold), and at 990 eV (above the L_2 threshold). The relative intensity $L\beta_1/L\alpha_{1,2}$ significantly depends on the incident photon energy and the target. The intensity ratio for the Cu target is constant at any incident photon energy. On the other hand, those for the Cu_2O and CuO targets are the highest at the L_2 threshold energy, decrease abruptly just after the L_2 threshold energy, and then increase with the incident photon energy. This tendency is of interest from the view of the chemical effects on the excitation and deexcitation processes for inner-shell electrons.

ACKNOWLEDGMENTS

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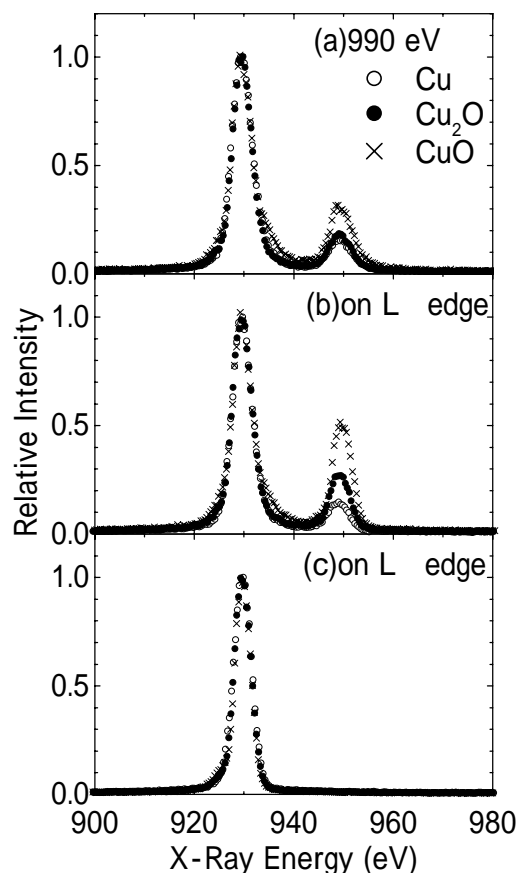


Figure 1. Comparison in the Cu L x-ray emission spectra of Cu, Cu_2O and CuO . Excitation energies are tuned at 990eV (a), L_2 (b) and L_3 (c) thresholds.

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Multi-Atom Resonant Photoemission Effects from Solid Surfaces and Free Molecules

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INTRODUCTION

In prior work at the ALS, it has been pointed out that a new type of interatomic resonant photoemission effect exists, and that this effect furthermore has the potential of providing a useful probe of near-neighbor atomic identities, bonding, and magnetism [1-5]. The phenomenon has been termed multi-atom resonant photoemission (MARPE). In measuring this effect, the photoelectron intensity of a given core level from atom "A" (e.g. O 1s from MnO) is monitored while the photon energy is tuned through a strong absorption edge for a core level on another atom "B" in the sample (e.g. the Mn 2p edges in MnO). Initial observations on MnO and other metal oxides appeared to show significant entirely-positive interatomic resonant effects in photoemission of up to 100% [1]. Additional measurements in Auger emission and soft x-ray emission from MnO seemed to confirm that such effects were also present in secondary decay processes as a result of resonant enhancement of the initial O 1s core hole formation [2]. A theoretical model for these effects based on the extension of intraatomic resonant photoemission ideas to the interatomic case was also developed and compared favorably with experiment [3]. Other measurements on transition-metal compounds [6] and an adsorbate-substrate system [7a] seemed to confirm these measurements and analysis.

Subsequently, it has been realized that such experimental measurements require very careful allowance for potential detector non-linearities [4,5,7b], since the observed electron intensities (particularly inelastically scattered backgrounds) change dramatically in going over any core resonance. In particular, the detector used for several of the first MARPE studies [1,2,4-7a], the standard microchannel plate-plus-phosphor-plus-CCD camera incorporated in the Gammadata-Scienta series of electron spectrometers, exhibits not only a typical saturation effect for high countrates, but also a strong quadratic component of counting that goes above linear for low countrates. Thus, spectra obtained in this low-countrate regime, while not exhibiting any kind of saturation effect, can be artificially enhanced in intensity in passing over a core-level resonance. Methods of accurately correcting spectra for these non-linearities have been discussed [4,5,7b, and abstract by Mannella et al. in this 2001 Compendium]. When these effects are allowed for, the magnitude of the effect is reduced and the form is found to change, with the shape usually involving a negative-then-positive swing in intensity reminiscent of a Fano profile in form [4,5,7b,8].

We here report more recent experimental results providing further evidence of such interatomic resonant effects in photoemission, for two very different limiting-case types of systems: a cleaved single-crystal oxide-NiO and a free molecule-SF₆. These data are discussed in terms of existing theoretical models for such MARPE effects [3,5], in particular, an x-ray optical (dielectric) approach that well describes the NiO data and a microscopic quantum mechanical model that should be useful in describing the SF₆ data.

EXPERIMENTAL PROCEDURE

The NiO measurements were performed on beamline 4.0.2 and made use of the Advanced Photoelectron Spectrometer/Diffractometer located there. Detector non-linearities were corrected for in all data presented here, using methods described elsewhere [4,5, and abstract in the 2001 Compendium]. A NiO single crystal was cleaved just before insertion into ultrahigh vacuum via a loadlock, then ion bombardment and annealing in oxygen to remove minor surface contaminant levels and assure correct stoichiometry before measurement. The incidence angle of the radiation was varied from grazing values of 5° to much higher values up to 40° (cf. experimental geometry in Figure 1(a)).

The SF₆ measurements were performed on beamline 8.0.1 and made use of a time-of-flight spectrometer described in detail elsewhere [9]. The detectors in this spectrometer are positioned in angle with respect to the incoming radiation and polarization vector such that non-dipole contributions to the angular distributions can be readily measured with high accuracy. For reference, the angular distributions of photoelectrons from a randomly oriented ensemble of free molecules is given by $d\sigma/d\Omega = (\sigma/4\pi)\{1 + \beta P_2(\cos\Theta_e) + [\delta + \gamma \cos^2\Theta_e] \sin\Theta_e \cos\Phi_e\}$, with β the dipole asymmetry parameter and δ and γ the first-order non-dipole parameters (cf. geometry in Figure 2(a), with Φ_e being the azimuthal angle around the polarization vector ϵ) [9].

EXPERIMENTAL RESULTS AND DISCUSSION

NiO(001): In Figure 1, we show experimental O 1s intensities from NiO as a function of photon energy and for five different x-ray incidence angles. For the lowest incidence angle of 5°, the effect of crossing the Ni 2p absorption resonances is dramatic, yielding a negative-then-positive excursion on crossing 2p_{3/2} whose amplitude is 75% of the intensity below the resonance. The magnitudes of these effects decreases as the incidence angle is increased, falling off to about 5% for an incidence angle of 40°.

Also shown in Figure 1 are theoretical curves based on an x-ray optical model of such effects, as discussed previously [5]. The optical constants that are key inputs for this model have been derived from concomitant partial-yield x-ray absorption measurements, with corrections for x-ray incidence angle and secondary electron takeoff angle [4], and subsequent Kramers-Kronig analysis [5]. The resulting theoretical curves are in excellent agreement with experiment for the lowest angle, and the agreement is very good for all other angles as well, although with some overprediction of the amplitudes at the higher angles. Non-zero effects are observed and predicted over the full angle range, in qualitative agreement with prior data for MnO [5]. These data thus disagree with one aspect of an earlier study of NiO by Finazzi et al. [8], in which they did not observe any sort of MARPE effect in O 1s emission from NiO; this lack of any effect appears to be due to measuring with too high an incidence angle and having insufficient statistical accuracy to resolve the small remaining effects seen, e.g. in Figures 2(e)-2(f).

We thus expect such MARPE effects to be observable in photoemission from any solid surface, with strength depending on the relative intensities of the absorption resonances. Furthermore, for homogeneous systems with flat surfaces, the x-ray optical model should provide a reasonably quantitative picture of the observed phenomena. Effects following an x-ray optical analysis have also recently been observed for photoemission from an adsorbate on a metal-N₂/Ni(001) [10]. For more complex cases with, e.g., three-dimensional nanometer-scale heterogeneity, the use of a microscopic model will be more appropriate.

SF₆: In Figure 2, experimental results for SF₆ are summarized. The x-ray absorption coefficient is shown in Figure 2(b), and the S 2p photoemission intensity and its asymmetry parameters were measured as photon energy was scanned across the "A" absorption resonance (corresponding to a F

1s t_{1u} -to- a^*_{1g} excitation). Although the total S 2p intensity (proportional to σ) does not show a significant change in crossing the resonance (\leq few %), the dipole asymmetry parameter β (as shown in Figure 2(b)) exhibits about a 15% excursion in magnitude that is also of the same general form as those in Figure 1. Similar effects are also seen in the parameters δ and γ [11].

Thus, interatomic resonant effects are also seen in this free molecule, and although they are too small to be observed as yet in the total intensity, they are clearly observed in the various asymmetry parameters. No theoretical calculations have as yet been performed for this case, but the x-ray optical model would clearly be inappropriate, and a microscopic approach such as that discussed previously [3,5] is the logical starting point for understanding these effects.

CONCLUSIONS

Multi-atom resonant photoemission effects are found in both the total intensities from homogeneous solid surfaces and adsorbates on such surfaces, for which an x-ray optical model is found to well describe the data, and in the angular distribution asymmetry parameters of a free molecule, for which a microscopic theoretical approach will be necessary. Similar effects in nanoscale structures will lie somewhere between these two cases.

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Figure 1. (a) Experimental geometry for measurements on Ni(001). (b)-(f) O 1s intensity as photon energy is scanned through the Ni 2p_{1/2-3/2} absorption resonances. Both experimental data (blue points) and theoretical calculations based on an x-ray optical model (red curves) are shown.

Figure 2. (a) Experimental geometry for measurements on gas-phase SF₆. (b) The x-ray absorption coefficient in the F 1s region as measured by partial electron yield. (c) The dipole asymmetry parameter β as photon energy is scanned through the "A" resonance in (b).

Figure 1.

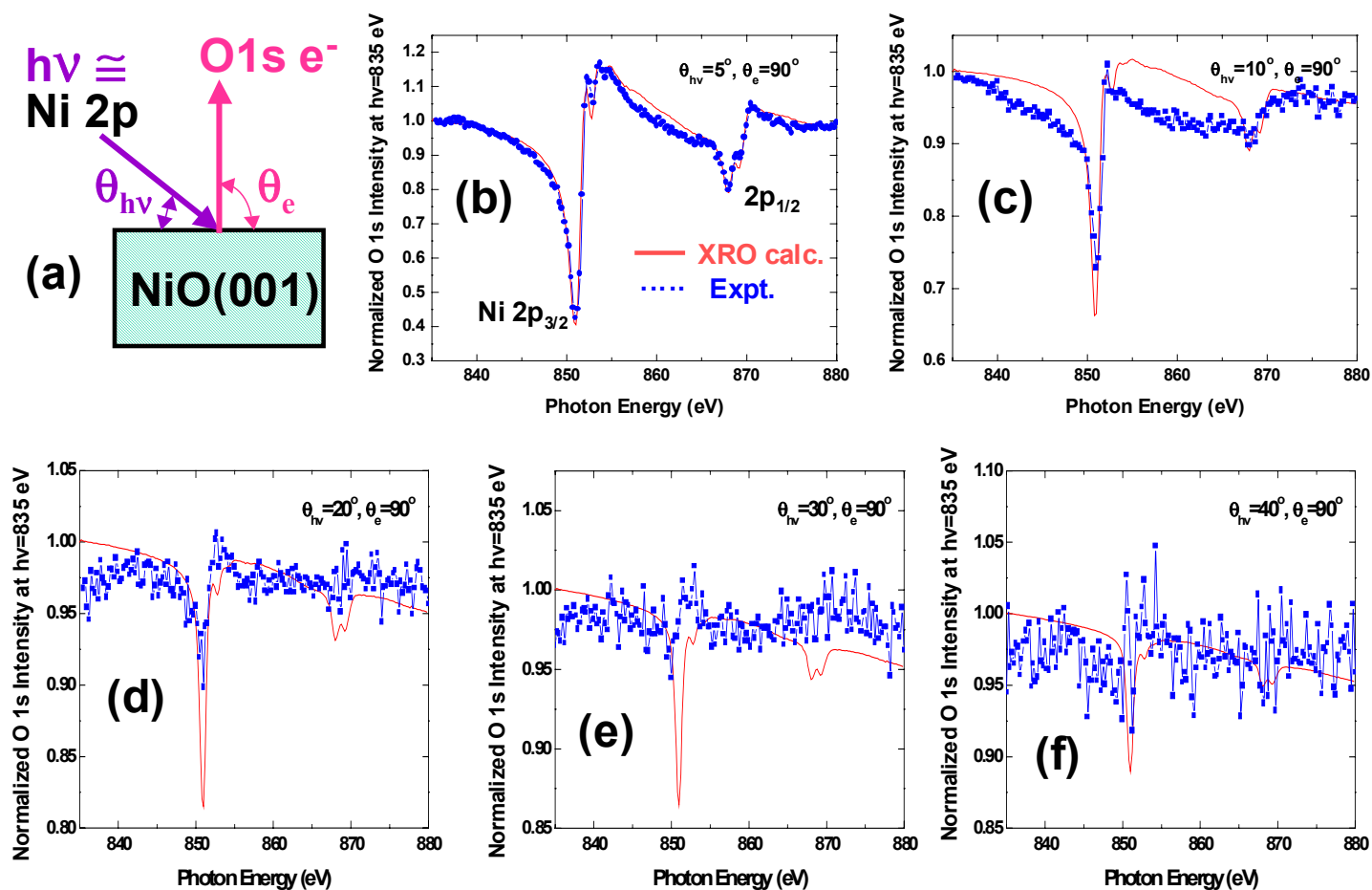
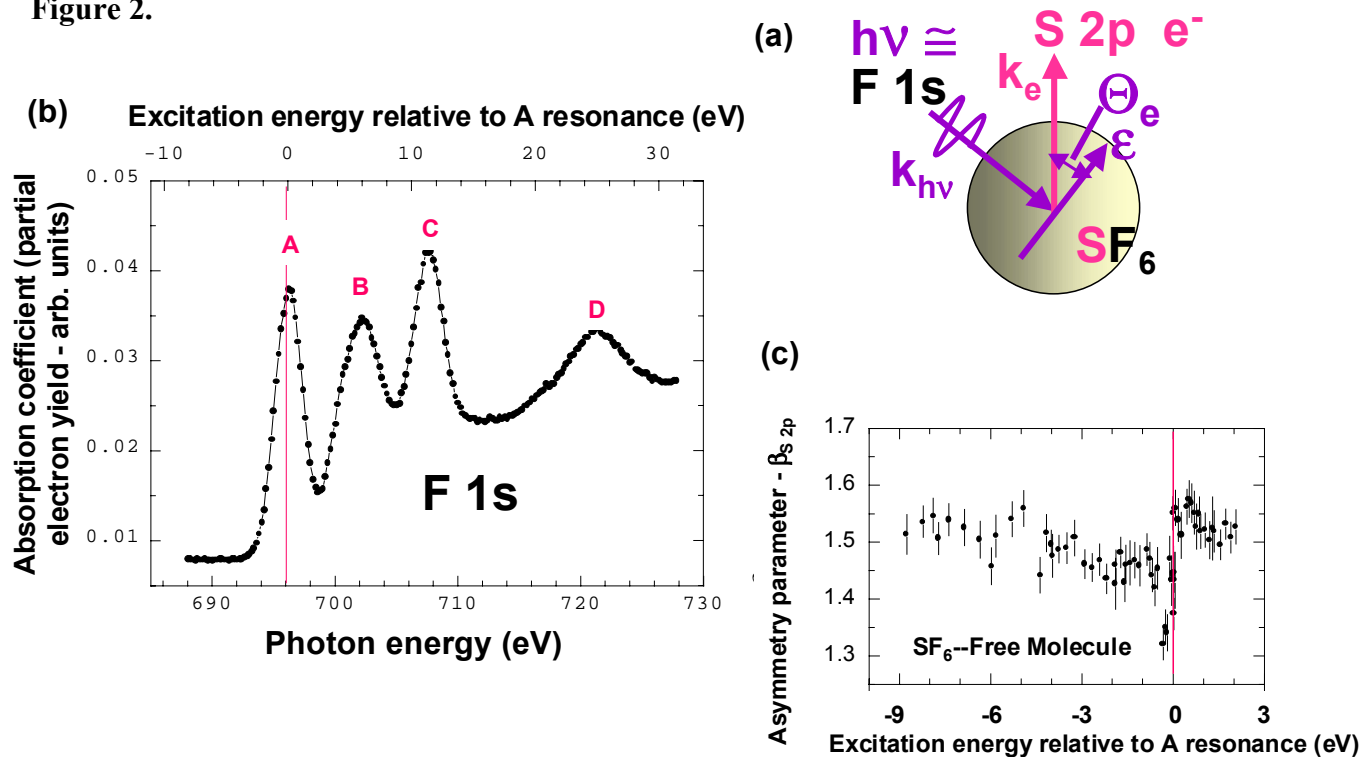


Figure 2.



VUV Photoionization of Superfluid Liquid Helium Droplets at the ALS

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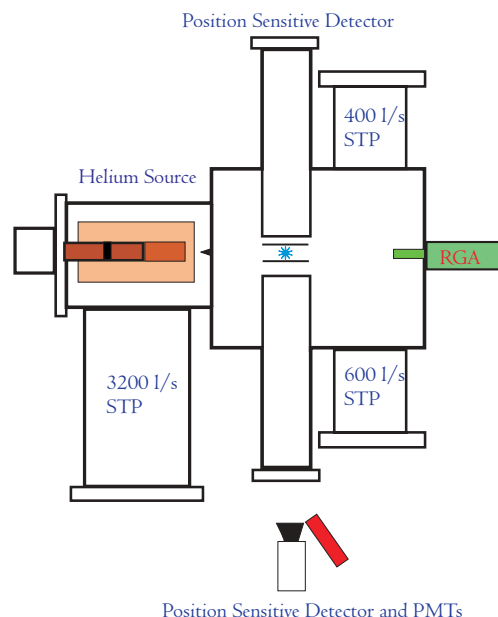
INTRODUCTION

Helium droplets have many interesting properties. They are very cold - evaporative cooling reduces the temperature to 380 milliKelvin. At these temperatures, the droplets are superfluid, and the electronic interactions between the He atoms can be described neither by He pair-potentials, nor by mean field theories. For an accurate description, quantum many body effects must be considered[1]. The complex interactions in the droplets will not affect only electronic excitations -relaxation processes will be altered as well. We have begun an in depth study of these processes near the helium atomic ionization threshold.

EXPERIMENTAL

The droplets were produced in a supersonic expansion using a 5 mm diameter nozzle aperture at typical He pressures of 15-50 bar and source temperatures of 11-18 K. The source conditions provided droplets with $\langle N \rangle = 10^4$ He atoms. The source chamber is pumped by a 3,200 l/s magnetically levitated turbo pump that is able to maintain a source pressure chamber of 10^{-4} with 60 bar, 13 K operation. The main chamber is evacuated by two magnetically suspended turbo pumps (Seiko Seike STP 600 and STP 400) backed by an oil-free scroll pump, providing 1000 l/s of pumping which keep the main chamber in the 10^{-7} 's during the experiment. VUV radiation from a 10 cm period undulator at the Advanced Light Source was dispersed by a 600 line/mm tungsten coated grating in a 3-m, normal incidence, off plane Eagle monochromator (McPherson). The endstation is schematically illustrated in the inset figure. The VUV light then ionized the droplets on the axis of a TOF spectrometer.

The generated photoelectrons then struck a 40-mm-diameter dual multi-channel plate (MCP), which is coupled to a phosphor screen (Galileo 3040FM) yielding positional information. The electron optics were biased to achieve "Velocity Map" conditions[2]. A photomultiplier tube monitored the light from the phosphor screen, allowing for total ion yield measurements. The recorded images are 2-dimensional projections of the 3-dimensional recoiling product electron sphere. Axial symmetry is maintained around the polarization axis, allowing reconstruction of the images using conventional inverse Abel transform techniques. The droplet beam was also detected by a residual gas analyzer (SRS RGA 200), which was mounted in the main chamber along the droplet propagation axis.



RESULTS and DISCUSSION

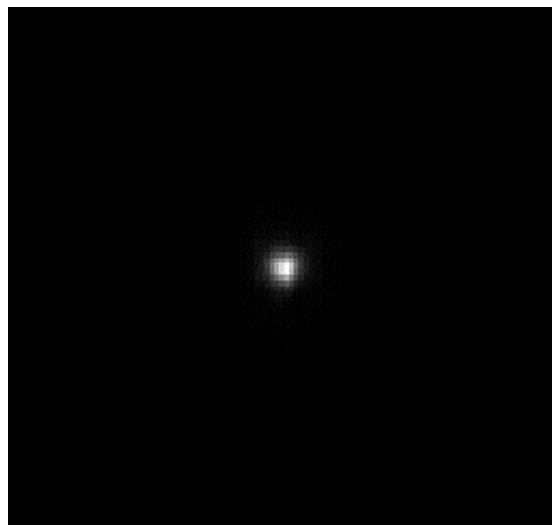
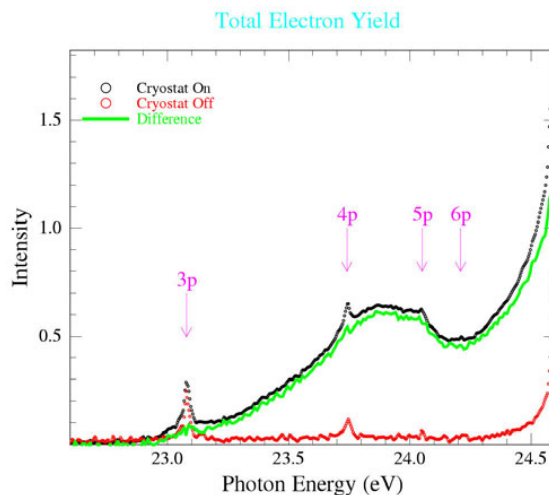
A photoelectron yield spectrum is shown to the right. The figure shows signal with the cryostat off - helium atoms only, the cryostat on - atoms and droplets, and the difference between the two. Also indicated in the figure are the atomic helium singlet np Rydberg energies converging the the helium ionization energy, 24.587 eV. Immediately one sees that the droplets ionization potential is suppressed relative to the atom.

The ionization process is mediated by the formation of He_2^+ which is bound by 2.35 eV relative to $\text{He} + \text{He}^+$. The photon energy required to access the minimum of the He_2^+ curve is ~ 22.2 eV. That the threshold for droplet ionization occurs $\sim .8$ eV above this is telling of the excitation process. In the droplets, the average distance between He atoms is ~ 3.6 Å. This is near the asymptotes of the He_2^* dimer potentials [3], thus it is expected that the excitations have significant atomic character. Using the atomic excitations as the zero order states of the droplets, we see the optically allowed excitation to He $(3p)^1P$ state is the first state of sufficient energy to allow for the production of He_2^+ . Our ionization onset is slightly below that of the atomic He $(3p)^1P$ state (23.08 eV), this could result from a combination of factors. In the droplet, multibody effects can perturb both the energy and symmetry of the states and couple states of differing angular momentum. [4]

Examination of the photoelectrons lets us probe the photoionization process in more detail. The electron leaves the droplet with near zero kinetic energy (< 10 meV), with an isotropic angular distribution. The isotropic distribution contrasts with the dipole allowed excitation, which with linearly polarized light would have a \cos^2 character. The electron angular and energy distributions change very little with large changes in photon energy (23-24.5 eV). This implies that the excitation process is distinct from the ionization process, and is indirect.

The initial excitation process generates essentially excited helium atoms in the droplets.

These can relax via fluorescence, the dominant process [5], or they can feel the influence of neighboring atoms in the droplet, leading to the formation on He_2^* . Because the poor coupling of He_2^* vibrational modes to those of the droplets, significant energy remains in the He_2^* [6]. These states are energetically degenerate with $\text{He}_2^+ + e^-$. We believe this results in vibrational autoionization of the He_2^* , and the subsequent generation of low kinetic energy electrons.



Photoelectron image following droplet excitation at 24 eV. The angular distribution is isotropic, and the electrons have near zero kinetic energy (small image radius)

CONCLUSIONS

The first dispersed photoelectron spectra from the ionization of helium droplets have been collected, giving insight into the ionization process in liquid helium droplets. The isotropic, near zero energy electrons implicate an indirect ionization process. Ionization below the atomic He threshold results from autoionization of $\text{He}_2^*(\text{He}_n)$ states. Further work is underway to examine the relaxation of the vibrationally excited He_2^+ remaining in the droplet, and processes occurring above the He atom threshold.

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VUV-IR Two Photon Ionization of Argon

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The first combination of infrared optical parametric oscillator (OPO) light source and synchrotron radiation (VUV region) has been introduced at Chemical Dynamics Beamline of the Advanced Light Source (ALS) associated with the Lawrence Berkeley National Laboratory. When the new technique VUV-IR double resonance combines with other detection method such as pulsed field ionization–zero kinetic energy photoelectron (PFI-ZEKE), photoelectron-photoion coincidence (PEPICO) and photo-induced Rydberg ionization (PIRI) spectroscopy etc., it becomes a very powerful tool to obtain high-resolution photoionization spectroscopic information. To demonstrate the well-alignment of the new set-up of the combined VUV-IR light source, two photon ionization spectra of argon have been recorded between the first ionization threshold ($\text{Ar}^+ \ ^2\text{P}_{3/2}$) and the second spin-orbit excited ionization threshold ($\text{Ar}^+ \ ^2\text{P}_{1/2}$). The autoionization Rydberg series of the np' and the nf' resonances have been observed up to principal quantum number of $n=57$, which is limited by the current IR beam bandwidth.

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